(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 19 September 2002 (19.09.2002)

(10) International Publication Number WO 02/073090 A2

(51) International Patent Classification7:

F23N

- (21) International Application Number: PCT/US01/50466
- (22) International Filing Date: 26 October 2001 (26.10.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/244,019 09/942,976 27 October 2000 (27.10.2000) US 29 August 2001 (29.08.2001) US

- (71) Applicant: CATALYTICA ENERGY SYSTEMS, INC. [US/US]; 430 Ferguson Drive, Moutain View, CA 94043
- (72) Inventors: DALLA BETTA, Ralph; 865 Doverton Square, Mountain View, CA 94043 (US). VELASCO, Marco, A.; 1476 Edsel Drive, Milpitas, CA 95035 (US). YEE, David, K.; 29070 Sebring Court, Hayward, CA 94544 (US). NICKOLAS, Sarento, G.; 1569 Park Ridge Drive, San Jose, CA 95118 (US).

- (74) Agent: HOLLAND, Charles, D.; Morrison & Foerster LLP, 755 Page Mill Road, Palo Alto, CA 94304-1018 (US).
- (81) Designated States (national): CA, CN, IN, JP, KR, RU.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Declarations under Rule 4.17:

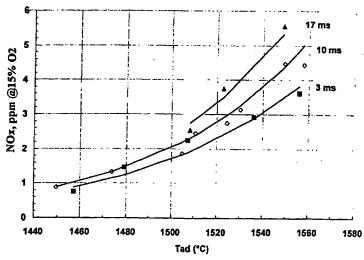
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations CA, CN, IN, JP, KR, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations CA, CN, IN, JP, KR, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL. PT, SE, TR)

Published:

without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: METHOD OF THERMAL NOX REDUCTION IN CATALYTIC COMBUSTION SYSTEMS



1440 1460 1480 1500 1520 1540 1500

Tad (°C)

(57) Abstract: Methods and apparatus, both devices and systems, for control of Zeldovich (thermal) Nox production in catalytic combustion systems during combustion of liquid or gaseous fuels in the post catalytic sections of gas turbines by reducing combustion the HC wave, principally by adjusting the catalyst inlet temperature. As the fuel/air catalytic sections of gas turbines by reducing combustion is reduced, the HC wave moves downstream (longer ignition delay time), shortens the local Nox production. The countervailing increase in CO production by the thermal Nox is reduced while power output while CO is maintained. <100 ppm, typically <50 ppm, and preferably <5-10 ppm.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/073090

PCT/US01/50466

METHOD OF THERMAL NOX REDUCTION IN CATALYTIC COMBUSTION SYSTEMS

INVENTORS:

RALPH A. DALLA BETTA MARCO A. VELASCO DAVID K. YEE SARENTO G. NICKOLAS

Field of the Invention:

The invention relates to methods and apparatus, both devices and systems, for control of NO_X in catalytic combustion systems, and more particularly to control of NO_X produced downstream of the catalytic reaction zone of a combustor, while at the same time maintaining the same power output yet low CO, by reducing combustion residence time, *inter alia*, through control of the location of the homogeneous combustion wave.

Background:

Gas turbines are used for a variety of purposes, among them: motive power; gas compression; and generation of electricity. The use of gas turbines for electrical generation is of particular and growing interest due to a number of factors, among them being modularity of design, generation output capacity to size and weight, portability, scalability, and efficiency. In addition, gas turbines generally use low sulfur hydrocarbon fuels, principally natural gas, which offers the promise of lower sulfur oxides or SO_X pollutant output. This is particularly important in urban areas that use, or can use, gas turbines for power generation, as they are attractive for power-grid supply in-fill to cover growing power needs as urban densification occurs.

Gas turbines tend to operate with a high turbine inlet temperature, in the range of from about 1100 °C for moderate efficiency turbines, to 1500 °C for modern high efficiency engines. To achieve these temperatures at the turbine inlet, the combustion system must produce a somewhat higher temperature, generally 1200 to 1600 °C as a result of some air addition due to seal leakage or the purposeful addition of air for cooling of portions of the gas turbine structure. At these temperatures, the combustion system will produce NOx. The amount of NOx produced increases as the temperature increases. However, to meet ever more stringent emissions standards, turbine operating conditions must be controlled so that the amount of NOx produced does not increase.

A typical gas turbine system comprises a compressor upstream of, and feeding compressed air to, a combustor section in which fuel is injected and burned to provide hot gases to the drive turbine located just downstream of the combustor. Fig. 1 shows such a prior art system employing a catalytic combustion system in the combustor section. Figure 1 shows a

conventional system of the type described in US patent 5,183,401 by Dalla Betta et al., US 5,232,357 by Dalla Betta et al., US 5,250,489 by Dalla Betta et al., US 5,281,128 by Dalla Betta et al., and US 5,425,632 by Tsurumi et al. These types of turbines employ an integrated catalytic combustion system in the combustor section. Note the combustor section comprises the apparatus system between the compressor and the drive turbine.

As shown in Fig. 1 the illustrative combustor section comprises: a housing in which is disposed a preburner; fuel source inlets; catalyst fuel injector and mixer; one or more catalyst sections; and a post catalyst reaction zone. The preburner burns a portion of the total fuel to raise the temperature of the gas mixture entering the catalyst, and some NOx is formed there. Additional fuel is introduced downstream of the preburner and upstream of the catalyst and is mixed with the process air by an injector mixer to provide a fuel/air mixture (F/A mixture). The F/A mixture is introduced into the catalyst where a portion of the F/A mixture is oxidized by the catalyst, further raising the temperature. This partially combusted F/A mixture then flows into the post catalyst reaction zone wherein auto-ignition takes place a spaced distance downstream of the outlet end of the catalyst module. The remaining unburned F/A mixture combusts in what is called the homogeneous combustion (HC) zone (within the post catalyst reaction zone), raising the process gases to the temperature required to efficiently operate the turbine. Note that in this catalytic combustion technology, only a portion of the fuel is combusted within the catalyst module and a significant portion of the fuel is combusted downstream of the catalyst in the HC zone.

Each type of drive turbine has a designed inlet temperature, called the design temperature. For proper operation of a gas turbine at high efficiency, the system or operator must control the outlet temperature of the combustor section to keep the temperature at the design-temperature of the drive turbine. This can be a very high temperature, in the range of 1100°C for moderate efficiency gas turbines and as high as 1400 to 1600°C for modern high efficiency engines. As shown in Fig. 1, at these high temperatures, NOx forms in the "Post catalyst reaction zone" of the combustor section. Although the NOx level produced in the post catalytic combustion zone is typically low for natural gas and similar fuels, it is still desirable to reduce this level even further to meet increasingly stringent emissions requirements.

Fig. 2 shows the relationship between the temperature in the post catalyst reaction zone and the amount of NOx produced, for a catalytic combustion system of the type shown in Fig. 1. At temperatures below about 1450 °C, identified in the figure as Region A, the level of NOx produced is below 1 ppm. As seen in Fig. 2, at temperatures above about 1450 °C, the Region B lower boundary, the NOx level rises rapidly, with 5 ppm produced at 1550 °C, and even higher levels above that temperature, on the order of 9-10 ppm or higher.

The formation of NOx at a high temperature is a kinetically controlled process. A portion of the NOx, called "Prompt NOx," or "Fennimore NOx," forms in the region of the combustor where rapid reactions occur. The amount of Prompt NOx formed depends on the fuel-to-air ratio and final flame temperature, but this Prompt NOx stops forming once the flame-front has consumed most of the fuel. A second pathway to the formation of NOx is the "Thermal NOx" or "Zeldovich pathway," in which NOx is formed continuously at high temperatures and in quantities dependant only on time and temperature. In typical gas turbine systems with residence times in the range of 10 to 20 ms (milliseconds), the prompt and thermal pathways produce roughly the same amount of NOx.

In most combustion processes, reaction of the fuel occurs in a flame that is fixed in location by a flame holder. The flame holder can be either a physical object or an aerodynamic process to anchor or stabilize the flame. Physical elements include bluff bodies, v-gutters, or other such mechanical parts that recirculate the gas stream to stabilize the flame. Aerodynamic stabilizers include physical elements such as swirlers and vanes and such modifications as expanded flow area to stabilize the flame. Flame temperature, temperature profile, physical dimensions of the combustor, and other such features determine the thermal NOx formation. For example, the designer cannot change thermal NOx levels without changing the volume or length of the combustor or the position at which the combustor design anchors the flame.

In the case of a catalytic combustion system using the technology described in the above-identified U S Patents, and other references, only a portion of the fuel is combusted within the catalyst and a significant portion of the fuel is combusted down stream of the catalyst in a post catalyst homogeneous combustion (HC) zone. Fig. 3 schematically illustrates the downstream HC zone.

The top portion of Fig. 3 is an enlarged schematic of a portion of Fig.1 showing the major components of a catalytic combustion system 12 located downstream of the preburner. The catalytic combustion system includes a catalyst fuel injector 11, one or more catalyst sections 13 and the post catalyst reaction zone 14 in which is located the HC (homogeneous combustion) zone 15. The bottom portion of Fig. 3 illustrates the temperature profile and fuel composition of the combustion gases as they flow through the combustor section described above. Temperature profile 17 shows gas temperature rise through the catalyst unit as a portion of the fuel is combusted. After a delay, called the ignition delay time 16, the remaining fuel reacts to give the full temperature rise. In addition, the corresponding drop in the concentration of the fuel 18 along the same path is shown as a dotted line.

As shown in the bottom portion of Fig. 3, a portion of the fuel is combusted, without flame, in the catalyst resulting in an increase in temperature of the gas mixture. The mixture

exiting the catalyst is at an elevated temperature and contains the remaining unburned fuel in air. This hot fuel and air mixture autoignites in a homogeneous combustion process in which the remaining fuel reacts in a radical reaction process to form the final reaction products of CO₂ and H₂O, and the temperature rises to the final combustion temperature for the total entering fuel and air mixture.

There is a similar problem with CO in the combustor output gases, in that regulations currently require less than about 100 ppm, and the movement is toward 10 ppm or less. A concern is that in reducing NOx levels, there may be a countervailing CO increase, such that in order to meet NOx limits, CO is exceeded. Thus, finding the window of low NOx and acceptable CO is increasingly difficult at the high Region B temperatures needed for efficient energy extraction.

Accordingly, for gas turbines that require combustor outlet temperatures in Region B in order to achieve the required drive-turbine design temperatures, and where emissions requirements demand NOx emissions levels below 3 ppm and CO on the order of 50 - 100 ppm or less, there is a need in the art for better control of the combustion process and ignition timing, and for improved combustion systems, apparatus and controls, in order to ensure that the NOx level produced in the combustion section of a gas turbine system can be maintained at lower levels, for example, 2 ppm or less while maintaining CO below about 10 ppm.

THE INVENTION

Summary, Including Objects and Advantages:

The invention comprises methods and apparatus, both devices and systems, for control of Zeldovich (thermal) pathway NOx production in catalytic combustion systems, and more particularly to control of NOx produced during combustion of liquid or gaseous fuels in the post catalytic sections of gas turbines by reducing combustion residence time in the HC zone through control of the HC wave, principally by adjusting the catalyst inlet temperature.

The invention arises out of the discovery that in the typical combustor having a physical or aerodynamic flame holder, the fuel and air mixture is combusted in a fixed position and does not move significantly as process conditions are varied. In contrast moreover, it has been discovered, unexpectedly, that in a catalytic combustor system, the location of the post-catalyst homogeneous combustion process that results in a temperature rise is not connected to the physical process or fixed flame holder, but rather is controlled by the catalyst exit gas conditions. Accordingly, the process of the invention comprises controlling the catalyst outlet temperature, which changes the HC wave location, which in turn controls the time period (residence time) during which the flame produces thermal NOx. As soon as the gas mixture enters the drive turbine, work is extracted and the gas temperature drops significantly and NOx

formation stops. Thus, in accord with the invention, by reducing the residence time at high post-catalyst reaction temperatures, NOx can be reduced to <3 ppm, preferably <2 ppm, while CO is maintained to within acceptable limits of <50 - 100 ppm, and even to <5 - 10 ppm.

This inventive feature is illustrated in Fig. 4, which shows a series of simple schematic drawings of a catalyst combustor system having a fuel injector, catalyst and post-catalyst homogeneous combustion zone feeding hot gas into a drive turbine. This series of figures illustrates schematically the change in the position of the homogeneous combustion wave, starting in Fig. 4A, with the HC wave being shown positioned downstream of the catalyst. The actual physical location of the HC wave is function of the ignition delay time, t_{ignition}, as shown in Fig. 3, and the gas velocity. In Fig. 4B, the ignition delay is adjusted to be very long, so that after the ignition occurs and the high temperature is reached, the time that the gas mixture will be hot enough for thermal NOx formation is relatively short and NOx formation will be minimized. In Fig. 4A the ignition delay time is at an intermediate value and in Fig. 4C the ignition delay time is very short. In each of these later cases, the Zeldovich pathway NOx formation is progressively higher due to progressively longer times in which the gas mixture is at the high post-combustion temperature.

The catalyst outlet temperature can be changed by changing the operating conditions of the combustor system. For example, in a first embodiment of the control aspects of the invention, the amount of fuel fed to the preburner (shown in Figure 1) is reduced, then the temperature entering the catalyst module will be lower and the temperature at the exit of the catalyst will also be lower. This lower temperature at the catalyst exit will move the homogeneous combustion wave farther downstream from the catalyst and closer to the turbine, thus reducing the level of thermal NOx formed. Similarly, increasing the fuel to the preburner will increase the catalyst outlet temperature, move the homogeneous combustion wave upstream and increase the amount of thermal NOx formed. Other control embodiments are described below in the Detailed Description section of this Application.

The inventive control of the location of the HC Wave to reduce the thermal NOx output is an unexpected and very unusual aspect of catalytic combustion systems employing the partial downstream combustion technology described here.

Brief Description of the Drawings:

The invention is described by reference to the drawings in which:

Fig. 1 is a schematic diagram of a typical prior art gas turbine showing the major components and using an integrated catalytic combustion system in the combustor section;

Fig. 2 is a graph of NOx produced vs Temperature in a catalytic combustion system and

showing low temperature, low NOx Region A, and the rapid increase in NOx produced in Region B above about 1450 °C;

Fig. 3 is a schematic diagram of a catalytic combustion system showing the post catalyst homogeneous combustion zone (HC Zone) located downstream of the catalyst in which the remaining portion of the fuel is combusted;

Fig. 4 is a multi-part schematic diagram of a catalytic combustion system showing changes in the position of the homogeneous combustion wave (HC Wave) in accord with the invention, Fig. 4A showing a general location, Fig. 4B showing long ignition delay moves the HC Wave further downstream toward the outlet to the turbine, and Fig. 4 C showing shortening the ignition delay moves the HC Wave toward the catalyst module;

Fig. 5 is a partial section, diagrammatic views of the test rig;

Fig. 6 is a graph of test results using the test rig of Fig. 5 showing NOx emissions as a function of residence time after essentially complete combustion of the fuel in the HC Zone;

Fig. 7 is a schematic diagram of a portion of the combustor down stream of the catalyst module showing exemplary locations for ultraviolet sensors in the post-catalyst reaction zone; and

Fig. 8 is a graph of the CO concentration profile, in ppm CO vs Residence Time, in the post catalyst reaction zone.

Detailed Description, Including the Best Mode of Carrying Out the Invention:

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives, and uses of the invention, including what are presently believed to be the best modes of carrying out the invention.

In this regard, the invention is illustrated in the several figures and tables, and is of sufficient complexity that the many parts, interrelationships, process steps, and sub-combinations thereof simply cannot be fully illustrated in a single patent-type drawing or table. For clarity and conciseness, several of the drawings show in schematic, or omit, parts or steps that are not essential in that drawing to a description of a particular feature, aspect or principle of the invention being disclosed. Thus, the best mode embodiment of one feature may be shown in one drawing, and the best mode of another feature will be called out in another drawing. Process aspects of the invention are described by reference to one or more examples or test runs, which are merely exemplary of the many variations and parameters of operation under the principles of the invention.

Fig. 5 shows a catalyst module 13, having two stages in series, of the type shown in US Patent 5,512,250, installed in a tubular test rig 70. Ambient air 72 is introduced at one end and hot exhaust gases exit the test rig at outlet 74 off one leg of an observation Tee 76. A thermocouple 78 measured the temperature of the air just downstream of an electric air heater 80. Thermocouples 82a and 82b were installed upstream and downstream of the catalyst module 13, respectively, to measure the gas temperature both upstream and just downstream of the catalyst module. Additional thermocouples 84 were located spaced various distances downstream of the catalyst module to progressively measure the temperatures of the gas in the homogeneous combustion zone downstream of the catalyst section. In addition, two water-cooled gas-sampling probes, P1 and P2, were installed in the reactor to measure the composition of the gas stream at the position thirty-three cm (P1) and fifty-three cm (P2) downstream of the catalyst. Fuel was supplied to preburner 86, and catalyst fuel 88 was introduced just upstream of a series of static mixers 90 to insure thorough Fuel/Air mixing.

The test sequence was as follows:

- 1. Set air flow 7900 SLPM (standard liters per minute) and the pressure to 209 psig.
- 2. Set air temperature to about 450°C.
- 3. Increase fuel flow necessary for post-catalyst reaction-zone temperature of 1400°C.
- 4. Vary the catalyst inlet temperature and the fuel flow to cover a variety of combustor outlet temperatures and to move the homogeneous combustion wave to various locations in the post-catalyst reaction-zone.
- 5. At each point where stable operation is obtained, hold the operating conditions constant and measure the concentration of NOx (NO plus NO₂), O₂, and CO₂.
- 6. The NOx concentrations are then corrected to 15% O₂ concentration by applying the equation (1) below where "ppm (test)" is the measured value of NOx, "O₂" is the concentration of O₂ at that measurement condition and "ppm (15% O₂)" is the NOx concentration corrected to 15% O₂.
- 7. NOx (ppm at 15% O_2) = NOx (ppm at test condition) X (20.9 15)/(20.9 O_2), Equation 1, with the results being shown in Fig. 6, NOx emissions in ppm as a function of the residence time after essentially complete combustion of the fuel.

The residence time shown for the different curves of Fig. 6 is the time from: 1) the point where most of the fuel has combusted and the temperature has risen to approximately the maximum post-catalyst reaction zone temperature, and 2) the point at which the gas sample is taken for measurement of the NOx level. The test was run by determining the homogeneous combustion wave location and then moving the location of this combustion wave by changing the inlet temperature of the fuel/air mixture to the catalyst by changing the power to the electric

air heater that heats the air in the test rig. As the catalyst inlet gases temperature is changed, the total fuel to the catalyst was changed to maintain a constant post-catalyst reaction zone temperature. As the fuel/air mixture inlet temperature (F/A temperature into the catalyst) is reduced, the homogeneous combustion wave moves downstream and shortens the residence time at high temperature. As the fuel/air mixture inlet temperature (F/A temperature into the catalyst) is increased, the homogeneous combustion wave moves toward the catalyst module and the residence time at high temperature increases. Over the entire temperature range studied, limiting the residence time to lower values reduces the NOx significantly. For example, at 1540°C, the NOx is reduced from 4.6 ppm to about 3 ppm or a reduction of 35%. At lower temperatures, the NOx level is lower, but operation at lower residence time still reduces the level of NOx.

On a gas turbine, the process by which the position of the homogeneous combustion wave can be controlled depends on the design of the catalytic combustion system. Where the catalyst inlet temperature is controlled by a flame burner, then the catalyst inlet temperature is controllable by changing the fuel flow to the flame burner. For example, in a fuel distribution proportioning embodiment of the invention, to decrease the level of NOx formed at a given turbine power output level where the drive turbine inlet temperature is to be held constant, the fraction of fuel fed to the preburner is decreased and the fraction of fuel fed to the catalyst fuel injector increased, so the total fuel fed to the gas turbine is held constant. Thus, by this proportional fuel flow control aspect of the invention, the total power output can be constant, yet since the fuel fed to the preburner has been decreased, the catalyst inlet and outlet temperatures are decreased and the homogeneous combustion wave is moved downstream to decrease the residence time at high temperature and the NOx level.

Other suitable processes for controlling catalyst inlet temperature will be evident to those skilled in the art for other combustor designs and for other combustion processes. Alternatively, holding the catalyst inlet temperature constant and varying the fuel to the catalyst also results in moving the homogeneous combustion wave. While this will also change the post-catalyst reaction zone temperature, that temperature change may be within an acceptable range for some combustion processes.

Additional embodiments of the inventive system and method that can be used to advantage in a system that is designed for, or takes advantage of, the control of the residence time at high temperature to control NOx, include the following:

• As shown in Fig. 7, one or more flame sensors 92 can be installed downstream of catalyst module in the post-catalyst combustion zone 14 of the combustor section 12 that are sensitive to the homogeneous combustion wave. For more detail on the location

and use of sensors, particularly optical sensors, in connection with control of gas turbines employing catalytic combustion systems, see our co-pending application USSN 09/942,976, filed August 29, 2001, entitled CONTROL STRATEGY FOR FLEXIBLE CATALYTIC COMBUSTION SYSTEM, the disclosure of which is hereby incorporated by reference. Exemplary sensors include various types of ultraviolet sensors that are sensitive to the radiation produced from at least some of the radical reactions that occur in the radical reaction process for hydrocarbon and other fuels. Such a UV sensor, such as 92a can be oriented to "look at" the outlet end of the catalyst module to protect it from over-temperature, as where the HC Wave encroaches on the catalyst module. A preferred position for a sensor is downstream adjacent the outlet to the turbine, as shown at the right of Fig. 7, where sensor 92b is positioned to be exposed to the homogeneous combustion wave when it is in the desired location. The signal of this sensor, or a series of such sensors disposed parallel to the longitudinal axis of the combustion zone, can then be used to control the combustion process, in particular to control the catalyst inlet temperature. e.g., by control of the F/A mixture entering the catalyst in accord with the inventive process to hold the homogenous combustion process in a particular, predetermined, desired location in order to limit the formation of NOx to a preselected level, e.g., to <3 ppm, preferably below about 2 ppm, and most preferably below about 1 ppm.

- A second type of sensor that can be used in a manner, and located in positions, similar to the above ultraviolet-type sensor, is an ion sensor whose signal is some function of the concentration of ionized gas molecules in the region near the sensor. Such sensors typically measure ion current between a pair of electrically charged plates or electrodes. Such a sensor, or array of suitably located sensors, can be positioned in the post catalyst reaction zone to monitor the location of the homogeneous combustion wave.
- Thermocouples can be located in post-catalyst reaction zone to measure gas temperature and thus the location of the homogeneous combustion wave, since the gas temperature rises substantially at the location of this combustion wave. Alternatively, thermocouples can be positioned to measure the combustion zone wall temperature (typically metal walls). Since the metal wall is in heat transfer relationship with the hot gases, the temperature rise in the gas at the location of the homogeneous combustion wave would be reflected as a corresponding temperature rise in the metal wall temperature.
- In cases where all of the operating parameters of the system are well understood and the important system parameters can be measured, then an empirical model of the combustor can be used to calculate the location of the HC Wave. This calculated value is then used in a control system algorithm to control the location of the HC Wave. This is an

example of a "model based control strategy".

- As the combustion wave moves very close to the combustor outlet or (turbine inlet), the CO level in the turbine exhaust may increase due to the fact that the reaction time in the HC Wave is too short to obtain complete reaction of the CO (oxidation to CO₂) within the combustor burnout zone. The CO concentration entering the drive turbine and also exiting the turbine exhaust will be as shown in Fig. 8, which is derived for a selected set of turbine and catalytic combustor operating conditions. The "knee" in the curve is at approximately 10 ppm CO, 13 ms Residence Time. Shorter residence times cause the CO to rapidly increase, while longer residence times can reduce the CO output to <10 ppm as shown in the curve. However, this is counter to the NOx curve, in that the shorter residence time means the HC Wave is closer to the catalyst unit with a corresponding longer residence time at high temperature in the post catalytic reaction zone, and more NOx is produced. Thus, the invention provides principles by which the operating parameters are adjusted by the controller to achieve this very difficult low NOx/low CO/high Power Output target window. Controlling the gas turbine so that the CO concentration is on the curve of Fig. 8, below about 100 ppm, and preferably in the vicinity of the knee in the curve of Fig. 8, <10 ppm and most preferably <5 ppm, still permits the HC Wave to be maintained at the desired location (residence time short, ignition delay long) for low NOx production. Thus, monitoring the CO level with CO sensors can be used to control the position of the HC Wave. The sensor 92b shown in Fig. 7 can be a CO breakthrough sensor, the readings of which are monitored and fed back to the controller, e.g., for F/A adjustment to control the HC Wave location. Alternatively, the CO sensor can measure the CO in the turbine exhaust (see Fig. 1) and the CO level sensor signal used as an input to a controller for control of the position of the HC Wave. One exemplary control strategy is to periodically change the combustor operating conditions so that the HC Wave is moved closer to or further away from the post catalyst reaction zone exit and monitor the CO level in the turbine exhaust. In this manner, the optimum operating conditions corresponding to a CO level in the range of 5 or 10 ppm CO can be determined and the turbine then can be controlled at this operating condition using an operating line control strategy as described in the aforesaid co-pending application SN 09/942,976 filed August 29, 2001, the disclosure of which is hereby incorporated by reference.
- Similarly, one or more NOx sensors in the HC Zone can be employed in locations as described above for Fig. 7. The sensor outputs are used to control the hot turbine inlet

gases to a specified NOx level by controlling the above-described parameters that adjust the position of the homogeneous combustion wave.

The actual location of the homogeneous combustion wave can be controlled by varying the following system or operating parameters:

- a. Changing the catalyst inlet temperature;
- b. Changing the fraction of air bypassing the catalyst to thus change the fuel/air ratio through the catalyst. Since the total turbine air flow and total turbine fuel flow is not changed, the turbine inlet temperature and load operating point will remain the same;
- c. Adjusting the air to the preburner, e.g., by overboard bleed of compressor discharge air upstream of the preburner which increases the fuel air ratio of the mixture in the catalyst and changes the position of the homogenous combustion wave;
- d. Changing the composition of the fuel mixture by adding or removing components that would effect the ignition delay time. Longer chain hydrocarbons or hydrogen, for example, will shorten the ignition delay time;
- e. Addition of water to the compressor inlet or to the combustor to increase total mass flow and thus modify the gas velocity and other operating conditions and thus change the position of the homogeneous combustion wave; and
- f. Fuel distribution proportioning as between the preburner and the catalyst module.

INDUSTRIAL APPLICABILITY:

It is clear that the process and apparatus of the invention will have wide industrial applicability, not only to catalytic combustion systems for gas turbines, but also to combustors employed in a variety of other types of power and hot gas producing systems, such as industrial boilers for steam and process heat.

The reduction in NOx while maintaining CO within acceptable limits and not sacrificing power output under the inventive process and apparatus is environmentally beneficial, offering the potential for significant amelioration in NOx produced by high temperature combustion processes, thus lending the invention a wide industrial applicability.

It should be understood that one of ordinary skill in the art can make various modifications within the scope of this invention without departing from the spirit thereof. It is therefore wished that this invention be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

WO 02/073090

PCT/US01/50466

CLAIMS:

- 1. In a method of combustion of a fuel/air mixture in a combustor having a catalytic combustion system containing a catalyst unit and wherein a portion of the fuel is combusted in a homogeneous combustion wave (HC Wave) downstream of said catalyst unit, said HC Wave being located in a post-catalyst reaction zone, said combustion producing hot combustion gases from which energy is extracted, the improvement comprising:
- a) controlling the location of said HC Wave in said post-catalyst reaction zone to reduce the time at which said hot gas is retained in said post-catalyst reaction zone before extraction of energy therefrom to reduce the NOx produced in said post-catalyst reaction zone.
- 2. A reduced NOx combustion process as in claim 1 wherein said NOx is reduced to below about 3 ppm in hot combustion gases having a temperature in the range of above about 1450 °C while maintaining the CO within the range of below about 100 ppm.
- A reduced NOx combustion process as in claim 2 wherein said combustor is part of a
 gas turbine system that includes a compressor upstream of said combustor providing
 compressed air to said combustor.
- 4. A reduced NOx combustion process as in claim 1 wherein said controlling step includes monitoring at least one condition of at least one of said fuel/air mixture and said hot combustion gas.
- 5. A reduced NOx combustion process as in claim 4 wherein said condition monitoring includes sensing at least one of fuel amount, fuel feed rate, fuel/air temperature, gases temperature, NOx, and CO.
- 6. A reduced NOx combustion process as in claim 5 wherein said NOx and CO is monitored and the location of said HC Wave is controlled to reduce NOx while maintaining CO within a predetermined range.
- 7. A reduced NOx combustion process as in claim 1 wherein said controlling step includes adjusting the catalyst outlet gas temperature to control the delay time for ignition of the fuel in the HC Wave.
- 8. A reduced NOx combustion process as in claim 7 wherein said catalyst outlet gas temperature is adjusted by controlling the temperature of the fuel/air mixture entering the catalyst.
- 9. A reduced NOx combustion process as in claim 8 wherein said combustor includes a preburner upstream of said catalyst unit and said tempera are of at least one of said fuel/air

mixture and outlet gas is controlled by at least one of:

- a) adjusting the fraction of air bypassing the catalyst;
- b) adjusting the fuel supplied to said combustor by proportioning the fuel supplied between said catalyst and said preburner;
 - c) adjusting air input to said preburner;
- d) changing the composition of the fuel by introduction of components that affect the ignition delay time; and
- e) addition of water in at least one of upstream of said combustor and in said combustor.
- 10. A reduced NOx combustion process as in claim 9 wherein the temperature of said hot combustion gas is maintained in a predetermined range for energy extraction and the fuel supplied to said preburner is controlled to move said HC Wave to a location to reduce NOx while maintaining CO to within a predetermined range of below about 50 ppm in said hot gas.
- 11. A reduced NOx combustion process as in claim 3 wherein said controlling step includes developing an empirical model of the operation of said combustor under a range of operating parameters, calculating the location of the HC Wave in the post-catalyst reaction zone as said parameters change, and setting system operating controls to selectively position the location of the HC Wave.
- 12. Apparatus for control of NOx produced during combustion of a fuel/air mixture in a combustor having a catalytic combustion system disposed medially therein and a post-catalyst combustion zone extending downstream of the catalyst of said catalytic combustion system, and a portion of the fuel is combusted in a homogeneous combustion wave (HC Wave) in said post-catalyst combustion zone, said combustion producing hot combustion gases from which energy is extracted, the improvement comprising:
- a) at least one sensor mounted in association with said post-catalyst combustion zone, said sensor outputting a signal responsive to at least one of said HC Wave, NOx, temperature and CO; and
- b) a controller receiving and processing said signal to control the location of the HC Wave to reduce the NOx produced in said post-catalyst combustion zone while maintaining CO levels to within a predetermined range in said hot gas.
- 13. NOx control apparatus as in claim 12 wherein said combustor is part of a gas turbine system that includes a compressor upstream of said combustor providing compressed air to said combustor and said NOx is reduced to below about 3 ppm in hot combustion gases having a temperature in the range of above about 1450 °C, and CO is maintained below about 100 ppm.

14. NOx control apparatus as in claim 12 wherein said controller adjusts the temperature of the catalyst inlet fuel/air mixture to control the location of said HC Wave.

- 15. NOx control apparatus as in claim 12 wherein said sensors are disposed in an array along at least a portion of said post-catalyst reaction zone to provide a profile of the sensed value in said zone.
- 16. NOx control apparatus as in claim 12 that includes at least one said sensor disposed in association with said combustor upstream of said catalyst.
- 17. NOx control apparatus as in Claim 12 wherein said at least one sensor is selected from at least one of a flame sensor, a UV sensor, an ion sensor, a CO sensor, and a temperature sensor.
- 18. NOx control apparatus as in claim 17 wherein at least one sensor is oriented to look at the downstream end of said catalyst.
- 19. NOx control apparatus as in claim 14 wherein said controller effects positioning of said HC Wave by:
 - a) adjusting the fraction of air bypassing the catalyst;
- b) proportionally feeding fuel supplied, between said catalyst and a preburner upstream of said catalyst in said combustor;
 - c) adjusting air input to said preburner;
- d) feeding fuel into said combustor having components that selectively affect the ignition delay time; and
- e) addition of water in at least one location selected from upstream of said combustor and in said combustor.
- 20. NOx reduction apparatus as in claim 13 wherein said controller includes an a control algorithm derived from an empirical model of the operation of said combustor under a range of operating parameters, said algorithm including calculated locations of the HC Wave in the post-catalyst reaction zone in relation to change in said parameters, and said controller sets system operating controls to selectively position the location of the HC Wave in response to at least one of selected hot combustion gas output temperature, NOx upper limit, and CO upper limit.

1/4

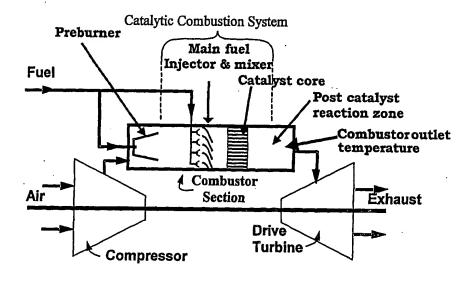


Figure 1, Prior Art

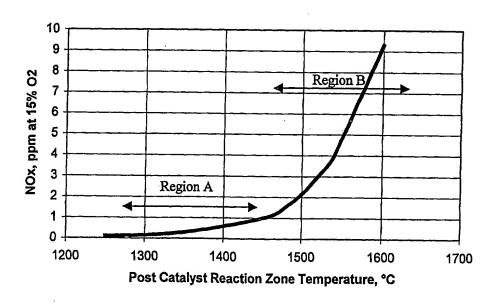
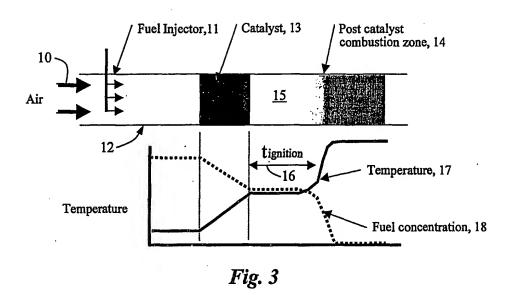


Figure 2, NOx produced vs. Temperature in a catalytic combustion system

2/4



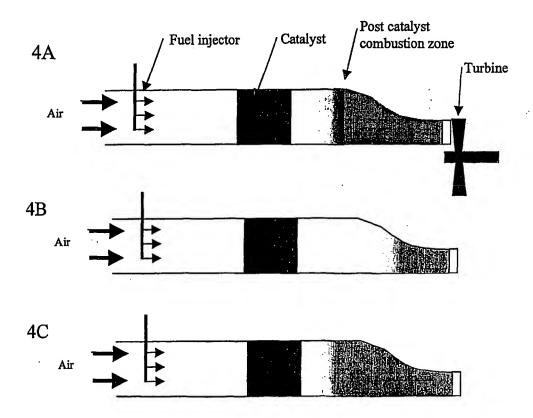


Fig. 4

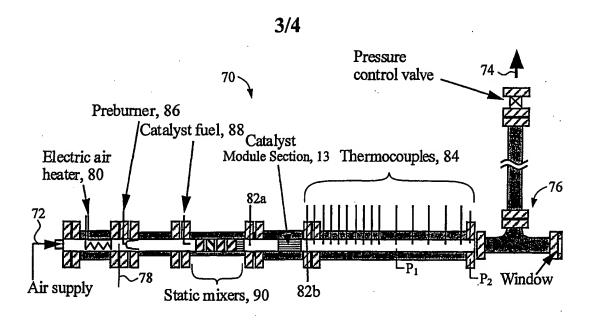


Fig. 5

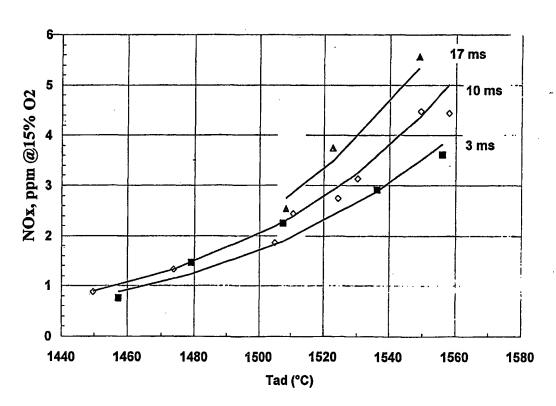


Fig. 6

4/4

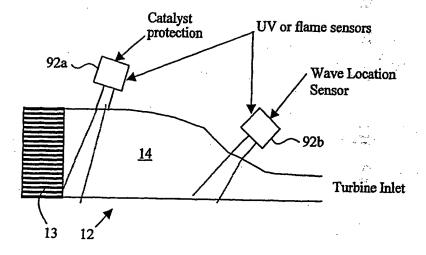


Fig. 7

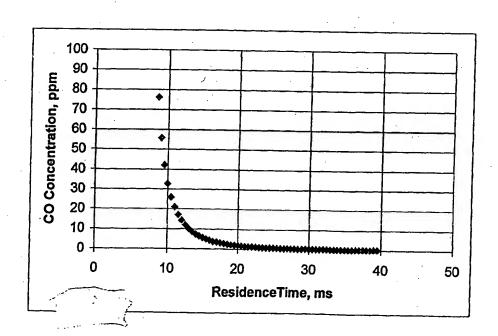


Fig. 8